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The Reaction of CuO with L-Ornithine

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Abstract

The reaction of CuO with L-ornithine in basic boiling water solution results in the formation of [bis-(1-pyrroline-2-carboxylate)copper(II)]·$8H_2O$. The complex, $C_{10}H_{28}CuN_2O_{12}$, $M_x = 431.9$ crystallizes in the monoclinic space group $P2_1/n$ with $Z = 2$. Cell dimensions are: $a = 6.849(4)$, $b = 20.552(4)$, $c = 7.291(4)$ Å, $\beta = 108.79(5)°$, $V = 971.6$ Å^3. The structure was refined to $R = 0.067$ and $R_w = 0.051$. The complex is centrosymmetric with the copper atoms at (0, 0, 0) and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ inversion centers. The geometry around the copper atom is essentially (4 + 2)-elongated octahedron. The ligand 1-pyrroline-2-carboxylate which is obtained by oxidation of L-ornithine to the corresponding α-keto acid followed by cyclization has a slight deviation from planarity. The water molecules of hydration form through hydrogen bonding a specially interesting three dimensional network in the crystal.

Introduction

Complexes of copper with amino acids have been studied extensively, and many have been prepared and structurally characterized [1].

We have been studying the complexation of Cu(II) with L-lysine, and have prepared and structurally characterized [bis(L-lysine)Cu(II)]Cl_2·$2H_2O$, [(L-lysine)$CuCl_2$]·$\frac{1}{2}H_2O$ [2] and [bis(3,4,5,6-tetrahydropicolinate)Cu(II)]·$8H_2O$ [3]. As has been previously suggested, the six-membered ring tetrahydropicolinate ligand is obtained in the presence of CuO by the oxidation of L-lysine to the corresponding α-keto acid followed by cyclization [3]. It was of interest for us to see whether L-ornithine will undergo in the presence of CuO a similar oxidation–cyclization reaction. Our results are reported in this paper.

Experimental

Synthesis of [Bis(1-pyrroline-2-carboxylate)copper-(II)]·$8H_2O$

A mixture of 5 g of L-ornithine·HCl and 2.5 g of CuO in 20 ml of distilled water was adjusted to pH 10 with NaOH. The resulting solution was refluxed for 5 h and then cooled to room temperature and filtered. Slow evaporation of the blue solution gave a blue precipitate which was dissolved in ethanol and filtered. Slow evaporation of the filtrate gave good quality crystals of the titled compound.

Crystallography and Structure Determination

Crystals of the complex were grown as dark blue prismatic plates which decompose almost instantaneously in the open air by losing their water of hydration. A single crystal of dimensions 0.1 × 0.3 × 0.3 mm was isolated from a batch of crystals under paraffin oil and quickly transferred to a glass capillary wetted with the same oil. The crystal was then mounted on a Philips 1100/20 four circle diffractometer and accurate cell parameters were obtained from 25 carefully centered reflections. Details of data collection and other crystallographic data are presented in Table 1.

Intensities were collected with graphite-monochromated Mo Kα radiation. Apparatus and crystal stabilities were monitored by three reference reflections. No fluctuations higher than 5% were detected. After the conventional corrections excluding absorption were applied, intensities were reduced to a list of structure factors.

The copper atom was located by a Patterson map at (0, 0, 0) and the remaining light atoms by successive difference Fourier maps. Calculations were performed by the SHELX 77 package [4]. Scattering factor tables for C, O and N were taken from Cromer and Mann [5], for H from Stewart *et al.* [6] and for Cu from the International Tables for X-ray Crystallography, Vol. IV. The correct assignment of the various atoms of the ligand was possible only at the final stages of the refinement. Hydrogen atoms were placed at their correct positions after all the non-hydrogen atoms were refined anisotro-

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TABLE 1. Crystallographic Data and Refinement Details

Formula	$Cu(C_5H_6O_2N)_2 \cdot 8H_2O$
Formula weight	431.9
$F(000)$	454
a	6.849
b	20.552
c (Å)	7.291
β (°)	108.79
V (Å^3)	971.6
Z	2
Space group	$P2_1/n$
D_c (g cm^{-3})	1.477
Radiation	Mo Kα
μ(Mo Kα) (cm^{-1})	12.29
Scan mode	$\omega/2\theta$
Scan speed (°ω min^{-1})	2
Scan width (°ω)	1.1
Angular range (2θ deg)	5–50
Monitor reflections	040; $\bar{1}21$; $1\bar{3}0$
Background time at each side of the peak (s)	10
No. unique reflections	1638
No. unobserved reflections	145
No. reflections at the final refinement stage	1259
Criterion for omission of F_{obs}	$F_o < 3\sigma(F_o)$
Number of refined parameters	171
R[a]	0.067
R_w[b]	0.063
Weighting scheme (w)	$3.575/(\sigma^2(F_o) + 0.005(F_o^2))$

[a] $R = \Sigma|\Delta|/\Sigma|F_o|$. [b] $R_w = \Sigma w^{1/2}|\Delta|/\Sigma w^{1/2}|F_o|$.

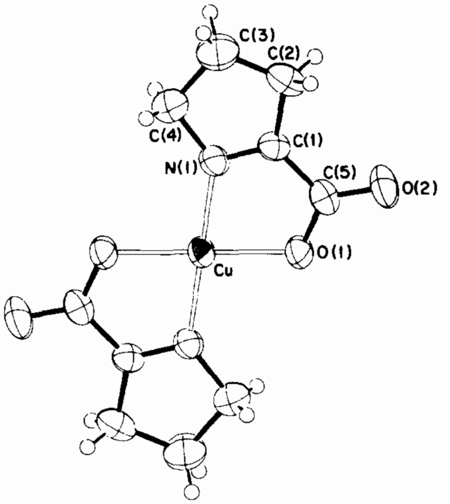

Fig. 1. Molecular structure and atomic labels of bis(1-pyrroline-2-carboxylate)Cu(II).

tropically. The structure was further refined by allowing the hydrogen atoms to shift isotropically. The positions of some of the water hydrogens were found dubious perhaps due to disorder. Unit weights were introduced at the initial stages and statistical weights at the final stages of the refinement. After convergence was reached $(\Delta/\sigma)_{max} < 0.8$ and the difference maps showed no electron densities higher than 0.5 e Å^{-3}. Final atomic coordinates are listed in Table 2.

An ORTEP [7] diagram of the complex is shown in Fig. 1, and a stereoscopic view of the packing of the unit cell is shown in Fig. 2. Important bond distances and bond angles are listed in Table 3.

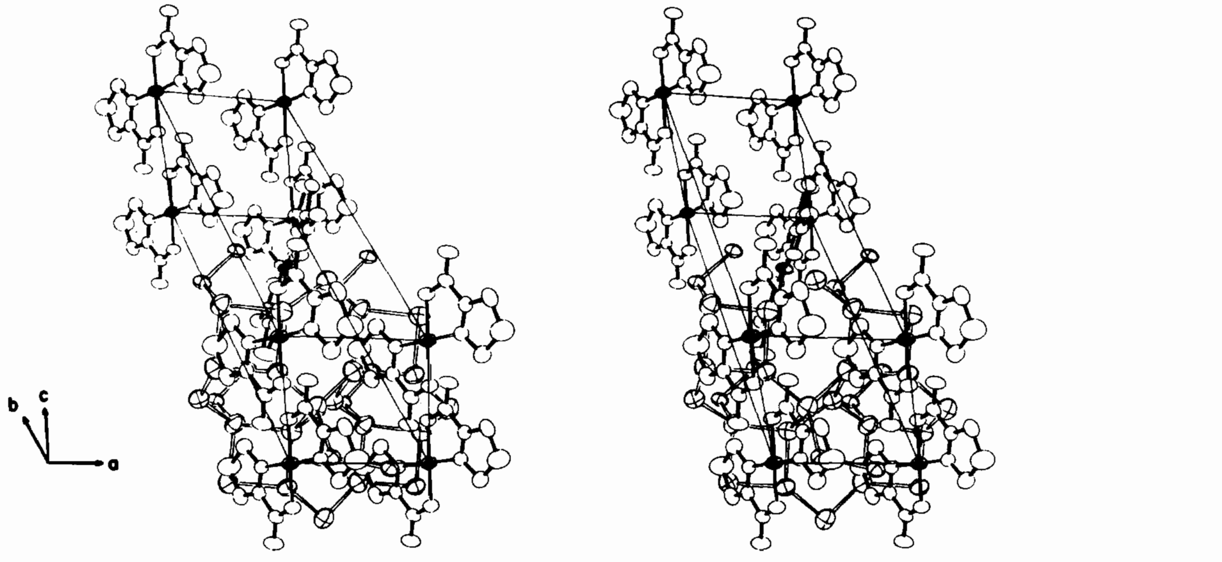

Fig. 2. ORTEP stereoscopic diagram of the crystal structure. Only a section of the hydrogen bonded pattern is shown for clarity. The water molecules are represented by 2A type ellipsoids.

TABLE 2. Final Positional Parameters for Non-hydrogen Atoms are $\times 10^4$ and for Hydrogens $\times 10^3$. Equivalent Temperature Factors (U_{eq})[a] are $\times 10^4$ Å^2 for All Non-hydrogen Atoms and Isotropic Temperature Factors (U_{iso}) are $\times 10^2$ [b]

Atom	x	y	z	U_{eq}
Cu	0	0	0	415(3)
C(1)	−2074(9)	425(3)	−3637(8)	359(14)
C(2)	−3112(13)	905(4)	−5166(10)	522(20)
C(3)	−3239(21)	1491(5)	−4015(14)	839(35)
C(4)	−2142(16)	1336(4)	−1927(12)	552(21)
C(5)	−1569(10)	−272(3)	−3884(9)	386(14)
N(1)	−1552(8)	643(2)	−1945(7)	388(12)
O(1)	−575(7)	−564(2)	−2304(5)	423(11)
O(2)	−2074(8)	−532(2)	−5491(6)	561(13)
OW(1)	−6668(10)	415(4)	−530(10)	553(17)
OW(2)	1169(16)	1918(4)	3001(14)	743(22)
OW(3)	3629(19)	1759(6)	482(18)	851(27)
OW(4)	2247(19)	2439(5)	6780(14)	875(24)
				U_{iso}
H(21)	−423(13)	76(4)	−597(12)	8(3)
H(22)	−228(11)	97(4)	−609(11)	8(2)
H(31)	−313(12)	181(4)	−417(12)	6(3)
H(32)	−503(19)	153(7)	−399(20)	20(6)
H(41)	−323(16)	131(5)	−144(15)	12(4)
H(42)	−112(12)	156(4)	−145(11)	6(2)
HW(11)	−665(13)	81(5)	−34(12)	8(3)
HW(12)	−694(17)	38(5)	−132(14)	10(5)
HW(21)	114(18)	148(6)	302(18)	15(5)
HW(22)	73(22)	206(6)	331(22)	15(7)
HW(31)	268(16)	190(5)	68(16)	9(4)
HW(32)	352(23)	157(6)	85(20)	10(6)
HW(14)	133(20)	272(7)	642(20)	20(6)
HW(42)	296(17)	259(6)	715(18)	7(6)

[a] $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij}a^*_i a^*_j(\mathbf{a}_i\cdot\mathbf{a}_j)$. [b] e.s.d.s given in parentheses.

The crystal structure of bis(1-pyrroline-2-carboxylate)Cu(II) consists of centrosymmetric units with the copper atoms residing on the (0, 0, 0) and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ inversion centers of the unit cell. The copper atom is bonded to two centrosymmetrically related ligands via the heterocyclic nitrogens N(1) and carboxyl oxygens O(1). Bond distances and bond angles in this structure are normal [1]. Two water molecules which are related by the inversion center occupy octahedral sites above and below the complex plane at a relatively long distance of 2.580 Å from the metal atom. Thus the geometry around the copper atom is best described as an elongated octahedron. The structure as a whole is quite similar to the one previously reported for the complex bis(3,4,5,6-tetrahydro-picolinate)Cu(II) [3]. The five-membered heterocyclic ring with the double bond located between C(1) and N(1) has slight distortion from planarity with bending about a line through C(2) and C(4). The carboxyl group is, as expected, coplanar with the ring portion defined by the atoms C(4), N(1) and C(1).

TABLE 3. Important Bond Lengths (Å) and Angles (°)[a]

Cu–N(1)	1.980(4)	C(5)–O(1)	1.283(6)
Cu–O(1)	1.974(3)	C(5)–O(2)	1.231(7)
C(1)–C(2)	1.487(9)	C(2)–H(21)	0.86(7)
C(1)–C(5)	1.498(8)	C(2)–H(22)	1.02(8)
C(1)–N(1)	1.251(7)	C(3)–H(31)	0.68(8)
C(2)–C(3)	1.49(1)	C(3)–H(32)	1.2(1)
C(3)–C(4)	1.50(1)	C(4)–H(41)	0.9(1)
C(4)–N(1)	1.481(9)	C(4)–H(42)	0.82(7)
N(1)–Cu–O(1)	82.4(1)	C(3)–C(4)–N(1)	104.2(7)
C(2)–C(1)–C(5)	128.1(6)	C(1)–C(5)–O(1)	114.5(5)
C(2)–C(1)–N(1)	114.6(5)	C(1)–C(5)–O(2)	121.6(6)
C(5)–C(1)–N(1)	117.3(5)	O(1)–C(5)–O(2)	123.9(5)
C(1)–C(2)–C(3)	102.4(7)	C(1)–N(1)–C(4)	111.2(6)
C(2)–C(3)–C(4)	107.4(8)		

[a] e.s.d.s given in parentheses.

In the unit cell, there are four independent water molecules per asymmetric unit. Three of them are involved in an unusual two dimensional hydrogen bonded networks which are extended to the third dimension by hydrogen bonds to the fourth water molecule. A section of this network is depicted in Fig. 3. Each two dimensional layer is extended parallel to the *ac* plane by the *n* glide planes and two translations along *a* and *c*. Its pattern is composed of squares and hexagons. Each square shares its edges with four hexagons. The linkage between the layers is formed by hydrogen bonds between OW(3) and OW(1).

The two dimensional hydrogen bonded network of water molecules can also be described in terms of one dimensional ribbons of alternating squares

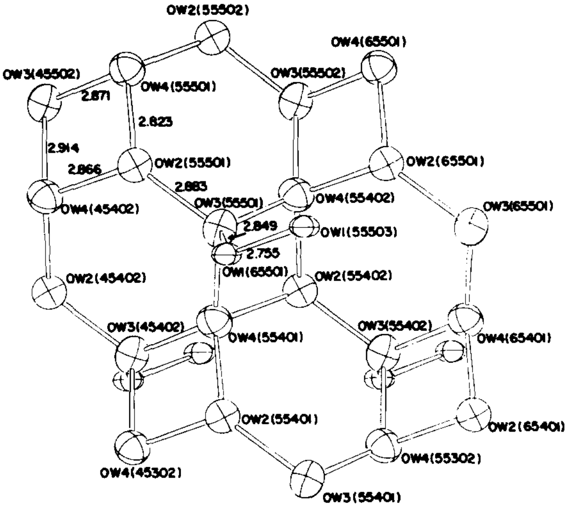

Fig. 3. A section of the hydrogen bonded pattern. The water molecules are denoted in parentheses by ORTEP codes.

and hexagons which are mutually shifted along the ribbon axis. Such a ribbon was found in the structure of bis(3,4,5,6-tetrahydro-picolinate)Cu(II) [3].

In a previous paper [3] we have shown that the reaction of CuO with L-lysine under certain conditions leads to the formation of the heterocyclic ligand 3,4,5,6-tetrahydropicolinate, a molecule which is implicated as an intermediate in the conversion of L-lysine to acetoacetyl–CoA [8]. It is believed that L-lysine is first oxidized to the corresponding α-keto acid by L-amino acid oxidase followed by cyclization to tetrahydropicolinic acid. We have therefore suggested that in an analogous way, CuO first oxidizes L-lysine to the α-keto acid which is then cyclized and trapped as the heterocyclic ligand by the copper atom. It was of interest for us to see whether L-ornithine will undergo a similar reaction leading to a five-membered heterocyclic ligand. We therefore reacted L-ornithine with CuO under similar reaction conditions and as expected isolated the cyclized product as a ligand by the copper atom. It is reasonable to suggest that the mechanism of this reaction is similar to the one described for the reaction of CuO with L-lysine.

Supplementary Material

Tables of anisotropic temperature factors and observed *versus* calculated structure factors are available from the author on request.

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